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Complexes of *N*-thiophosphorylthioureas RNHC(S)NHP(S)(O*i*Pr)$_2$ (HL) (R = pyridin-2-yl, pyridin-3-yl, 6-amino-pyridin-2-yl) with copper(I): Crystal structures of Cu(PPh$_3$)$_n$L (n = 1, 2)

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ABSTRACT

Reaction of the potassium salts of *N*-thiophosphorylated thioureas of common formula RNHC(S)-NHP(S)(O*i*Pr)$_2$ [R = pyridin-2-yl (**HL^a**), pyridin-3-yl (**HL^b**), 6-amino-pyridin-2-yl (**HL^c**)] with Cu(PPh$_3$)$_3$I in aqueous EtOH/CH$_2$Cl$_2$ leads to mononuclear [Cu(PPh$_3$)$_2$L^{a,b}–*S*,*S*′] (**1**, **2**) and [Cu(PPh$_3$)L^c–*S*,*S*′] (**3**) complexes. Using copper(I) iodide instead of Cu(PPh$_3$)$_3$I, polynuclear complexes [Cu$_n$(L–*S*,*S*′)$_n$] (**4–6**) were obtained. The structures of these compounds were investigated by IR, ^{1}H, ^{31}P{^{1}H} NMR spectroscopy, ES-MS and elemental analyses. The crystal structures of Cu(PPh$_3$)$_2$L^b (**2**) and Cu(PPh$_3$)L^c (**3**) were determined by single-crystal X-ray diffraction.

1. Introduction

There is a growing family of R$_2$P(X)NHP(X)R′$_2$ polynuclear aggregates of common formula [M$_3${R$_2$P(X)NP(X)R′$_2$}$_3$] (M = Cu(I), Ag(I); X = S and Se) with a cyclic M$_3$X$_3$ core [1–3] and ionic complexes [M$_4${Ph$_2$P(X)NP(X)Ph$_2$}$_3$]$^+$An$^-$ with a tetrahedral M$_4$ core surrounded by six chalcogen atoms [4,5]. Contrary to the previously mentioned ligands, there is a lack of information about structures of the polynuclear copper(I) complexes containing *N*-thiophosphorylated thioureas and thioamides, RC(S)NHP(S)R′$_2$ [6–9].

On the other hand heteroligand copper(I) complexes of triphenylphosphine and XCNPY or XPNPX (X, Y = O, S, Se) backbone ligands [10–13] have been earlier reported. It was established that PPh$_3$ was used as an additional donor ligand to prepare the non-cluster complex of Cu(I), where the copper atom is bound only to one molecule of chelating SPNPS ligand [12]. In this case, the filling of coordination sites of copper(I) is necessary to prevent cluster formation.

Published data reveal that structure and properties of triphenylphosphine containing complexes of XCNPY or XPNPX are strongly dependent on the nature of chelating ligand. To the best of our knowledge there are no data explaining reasons of one or two PPh$_3$ molecules binding with Cu(I) metal centre. For this purpose we conceived to use thiophosphorylated thiourea, containing sterically demanding substituent capable to the hydrogen bonds formation.

In this work, we describe the synthesis and structural characterization of several new polynuclear complexes of the Cu(I) cation with *N*-thiophosphorylthiourea ligands RNHC(S)NHP(S)(O*i*Pr)$_2$ [R = pyridin-2-yl (**HL^a**), pyridin-3-yl (**HL^b**), 6-aminopyridin-2-yl (**HL^c**)] (Chart 1) and their mononuclear analogues containing triphenylphosphine ligands. Complexes of monovalent copper are of interest as catalysts of numerous processes including homolytic C–Hal (Hal = Cl and Br) bond cleavage in polyhaloalkanes [14–17]. Catalytic properties of complexes obtained will be published as separate article.

2. Experimental

N-Thiophosphorylated thioureas **HL$^{a–c}$** were prepared as previously described [18,19] and purified by recrystallization from dichloromethane to *n*-hexane mixtures.

2.1. Synthesis of Cu(PPh$_3$)$_n$L$^{a–c}$ (**1–3**)

A suspension of **HL$^{a–c}$** (1 g, 3 mmol) in aqueous ethanol (15 mL) was mixed with an ethanol solution of KOH (0.185 g 3.3 mmol). A dichloromethane (15 mL) solution of Cu(PPh$_3$)$_3$I (2.934 g, 3 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further hour and a precipitate was filtered off. The filtrate was

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